

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 8/12, C09D 129/04, 131/02, G03F 7/09	A1	(11) International Publication Number: WO 98/13394 (43) International Publication Date: 2 April 1998 (02.04.98)
(21) International Application Number: PCT/US97/17761 (22) International Filing Date: 29 September 1997 (29.09.97) (30) Priority Data: 196 39 897.5 27 September 1996 (27.09.96) DE (71) Applicant (for all designated States except US): SUN CHEMICAL CORPORATION [US/US]; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): BAUMANN, Harald [DE/DE]; Obere Herrentalstrasse 8, D-37520 Osterode (DE). DWARS, Udo [DE/DE]; Schlossstrasse 9, D-37412 Herzberg (DE). SAVARIAR-HAUCK, Celin, M. [DE/DE]; Am Breitenberg 14, D-37534 Badenhausen (DE). PAPPAS, Socrates, Peter [US/US]; 205 Jay Street, Wood-Ridge, NJ 07075 (US). TIMPE, Hans-Joachim [DE/DE]; Baumhofsstrasse 165, D-37520 Osterode (DE). (74) Agent: PERSLEY, Sidney; 222 Bridge Plaza South, Fort Lee, NJ 07024 (US).	(81) Designated States: US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SF). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: WATER SOLUBLE AND OXYGEN-IMPERMEABLE POLYMERIC LAYERS (57) Abstract Water soluble oxygen-impermeable coatings possessing high photosensitivity, good resolution, good ink receptivity after development, long shelf life and good adhesion. The amine- and hydroxy-functional vinyl coatings are to be used in the production of lithographic printing plates.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NI	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

5

WATER SOLUBLE AND OXYGEN-IMPERMEABLE POLYMERIC LAYERS

Field of the Invention

10 The invention relates to water soluble and oxygen impermeable polymeric layers used in photosensitive materials.

Description of the Related Art

15

Water soluble polymers are used as temporary coatings on organic photosensitive substrates. They are also used, for example, in manufacturing offset printing molds, letterpress plates, litho plates for screen
20 printing, printed boards and in etching preforms.

In the uses stated above the water soluble polymers have the function of protecting the substrate from aerial oxygen during storage, exposure and particularly during
25 the period between exposure and further processing (development and the like). During this period the temporary coating has to exhibit a sufficient adhesion to the photosensitive substrate so that a safe handling (manufacture, packing, transport, exposure etc.) is
30 guaranteed such that the layers are not torn. On the other hand it must easily be possible to remove the temporary coating before development, at best by washing with water.

35 A plurality of water soluble polymers were tested in practice. It was found that polymers such as polyvinyl alcohol, partly saponified polyvinyl acetate, which can also contain vinyl ether and vinyl acetal units, polyvinyl pyrrolidone and copolymers thereof with vinyl
40 acetate and vinyl ethers, hydroxy alkyl cellulose,

gelatin, polyacrylic acid,² gum arabic, polyacrylic amide, dextrin, copolymers of alkyl vinyl ethers and maleic acid anhydride as well as water soluble high molecular polymers of ethylene oxide having a molecular weight of
5 above 5000 are particularly suitable. This is due to the low oxygen permeability of these polymers, compare measured values in K. Petrak, E. Pitts, J. Appl. Polym. Sci. 25 (5) pages 8789 - 886. Polyvinyl alcohol is particularly suitable. However, many of the polymers
10 prove to be insufficient in their adherence to organic, photosensitive, substrates. For example, polyvinyl alcohol layers can easily be removed by means of adhesive tapes or by cutting substrates coated with polyvinyl alcohols, the water soluble protective coating often
15 peels off easily at the edge the cut.

Furthermore it was found that some water soluble polymers used as coatings affect specific properties of the photosensitive layers such as include photo-
20 sensitivity, resolving capacity and thermal stability in storage. A number of tests have been carried out to improve the properties of the water soluble protective layers on organic photosensitive substrates.

25 U.S. Patent 3,458,311 describes coating a water soluble overcoat in the presence of a solvent mixable with water for the provision of adherence. However, the adhesion capacity is only improved to a minor extent because of the high solvent content. Thus, the
30 components of the photosensitive layer are easily removed, which impairs the function of this layer considerably.

U.S. Patents 4,072,527 and 4,072,528 disclose
35 polymer coatings dissolved in water having insoluble polymers dispersed therein. However, the removability of the resulting coatings by aqueous media is reduced along with the shelf life of the materials.

3

U.S. Patent 4,942,111 describes amphoteric compound additives to water soluble coatings. However, the adhesion of the coatings is too low.

5 U.S. Patent 4,988,607 describes coatings which contain a maximum of 20 wt.% of photoinitiators. However, only water soluble initiators can be introduced into the coating. Furthermore, the adherence and thermal stability of the system is not improved.

10

The situation is similar when antihalation dyes are introduced into the coating according to European Patent 354 475 or polymerization inhibitors according to U.S. Patent 5,254,437. Slightly improved sharpness of the photosensitive layer is obtained while photosensitivity is reduced and the poor adhesion of the coatings remains.

15

U.S. Patent 5,273,862 discloses the combination of a water soluble polymer having a low aerial oxygen permeability with an aerial-oxygen-binding water soluble polymer. Polymers with aliphatic amino groups, preferably polyalkylene imines, are mentioned as aerial-oxygen-binding polymers. However, such combinations prove to be unsuited for the practical use, because amino-group containing polymers exhibit a high tendency to absorption at the surface of the photopolymer. Therefore the photopolymer surface remains hydrophilic, even after the development, which results in poor ink receptivity on plates made with these polymers.

25

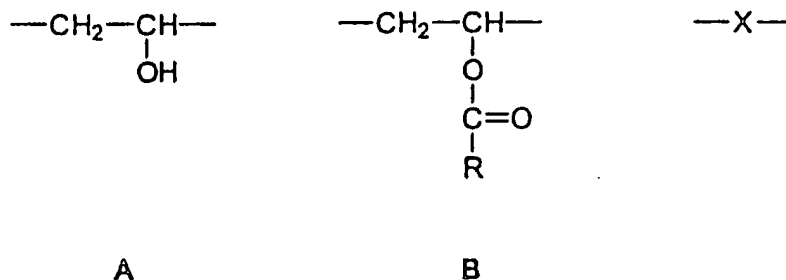
30

An object of the present invention is to provide water soluble oxygen-impermeable coatings which, when used in photosensitive lithographic printing plates, not only result in a high photosensitivity (independent of the outside air pressure), good resolution, good ink receptivity after the development, but above all, guarantee long shelf life of the lithographic plate and good adhesion to the organic substrate.

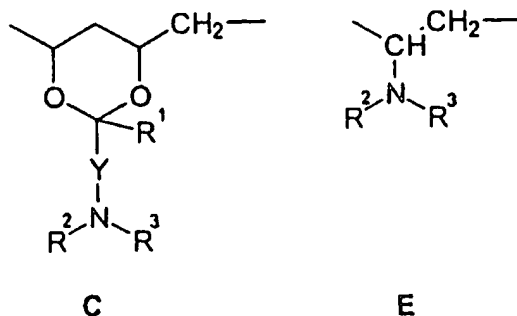
35

Summary of the Invention

The invention is a coating containing a polymer consisting of a binder having the following units:



wherein R is a C₁-C₈ straight-chain or a branched alkyl and the X comprises an amino group that is connected to the polymer chain either directly or via a spacer and is comprised of at least one of two structures below:



wherein R¹, R² and R³ are independently selected from hydrogen, alkyl, aralkyl or aryl and Y is an aliphatic, aromatic or araliphatic spacer group.

Detailed Description of the Invention

The coatings according to the invention, which exclusively consist of the polymer according to the invention, exhibit a low oxygen permeability even if the

5

layers are very thin. This property is particularly due to the amount of binder units A and B described above.

5 The particular advantage of the coatings according to the invention is their extremely good adhesion to organic substrates. This adhesion is especially strong when the organic substrates contain polar groups such as carboxyl groups. This adhesion is obtained above all by the basic, nitrogen-containing binder units C in the
10 polymer according to the invention.

The basic amino groups are especially suitable due to their provision of adhesion. The amino groups may be primary, secondary or also tertiary.

15

By means of varying the amount of the basic, nitrogen-containing groups in the water soluble polymer, the adhesion capacity can be adapted according to the corresponding adhesion problem in practice. It is proven
20 that the water soluble coatings according to the invention contain polymers consisting of 10 to 98 wt.% of binder unit A, 0.1 to 30 wt.% of binder unit B and 0.1 to 60 wt.% of X.

25 Polymers, according to the invention, suitable as a binder in coatings may contain other compounds such as rheological additives, foam separators, dyeing agents, stabilizers and/or preservatives, but also other polymers or copolymers such as polyvinyl alcohol, gelatin or
30 hydroxy alkyl cellulose, and other polymers known to one skilled in the art as oxygen-impermeable compositions.

There are basically two different ways to introduce the basic nitrogen-containing binder unit X into the
35 polymers of the water soluble coatings of the invention. Namely, (a) the copolymerization with nitrogen-containing monomers and optionally further reactions with the polymer and (b) the reaction of polymers with nitrogen-containing low molecular compounds.

In preparing the polymers of the water soluble coatings of the invention by copolymerization, generally a vinyl ester is copolymerized with the nitrogen-
5 containing monomers; subsequently the ester groups are saponified to the desired extent by acid or alkaline saponification, then the product is isolated. The polymerization, saponification and isolation steps are carried out according to processes well-known to those of
10 ordinary skill in the art. A particularly preferred process is where vinyl acetate which is free radical polymerized with the nitrogen-containing monomers.

Frequently, it is preferable to start with nitrogen-
15 containing monomers in which the amino groups are present in a protected form, so that no undesirable side reactions take place during the polymerization step. A preferred way of protecting the amino groups is by acylation. Especially preferred is acylation with a
20 formyl or acetyl group. The protective groups of this type are particularly advantageous since they are removed in the saponification step of, for example, a vinyl acetate group.

25 The free radical copolymerization of vinyl acetate with N-vinyl acetamide or N-vinyl formamide and their saponification, resulting in a polymer consisting of vinyl alcohol, vinyl acetate and vinyl amine, proved to be especially suitable and economical.

30

The second method for making the polymers coatings under the invention involves, commercially available, almost completely or partly saponified, polyvinyl ester, simply referred to as "polyvinyl alcohol". It is
35 modified by a reaction analogous to a polymer reaction. This is an especially suitable way to form the binder unit embodied by structure C of amino group containing aldehydes or their acetals. The polyvinyl alcohols preferably used for synthesis in the present invention

have a residual content of esterified groups in the range of between 0.1 to 30 wt.%. Especially preferred are polyvinyl alcohols prepared from polyvinyl acetate, i.e. R = CH₃ in binder unit B, having a residual acetate content of between 1.5 to 22 wt.%. The adhesion capacity as well as the water solubility of the coatings according to the invention is influenced by the molecular weight of the polyvinyl alcohols used for the synthesis. A lower molecular weight promotes the removal of the coating by water, or in the case of lithographic plates by means of aqueous alkaline developers. The use of polyvinyl alcohols exhibit viscosities of between 2 and 26 mPa·s as 4% aqueous solution in water at 20°C.

The amino group containing aldehydes or acetals of amino group containing aldehydes are reacted with polyvinyl alcohols according to standard processes known per se forming acetal structures (corresponding to structure C). Examples of amino group containing aldehydes or acetals of amino group containing aldehydes are: 2-amino acetaldehyde dimethyl acetal, 2-amino acetaldehyde diethyl acetal, 2-N-methyl amino acetaldehyde diethyl acetal, 2-N-methyl amino acetaldehyde dimethyl acetal, 4-amino butyraldehyde dimethyl acetal, 4-amino butyraldehyde diethyl acetal, 2-amino propionaldehyde dimethyl acetal, 2-amino propionaldehyde diethyl acetal, 4-N,N-dimethyl amino benzaldehyde and 4-N,N-diethyl amino benzaldehyde.

This reaction generally requires the addition of a strong inorganic or organic catalytic acid. Examples of catalytic acids include hydrochloric acid, sulfuric acid, phosphoric acid and p-toluene sulfuric acid. An especially preferred catalytic acid is hydrochloric acid. The amount of the acid added preferably ranges from 1 to 25 wt.% depending on the amount of polyvinyl alcohol used.

6

The reaction temperature of the acetalization depends on the type of aldehydes employed as well as the desired degree of reaction. The reaction temperature is preferably between 0°C and the boiling point of the solvent used. More preferably, the reaction temperature
5 ranges between 5°C and 100°C.

Water and organic solvents as well as mixtures of water with organic solvents are used as acetalizing
10 solvents. Particularly suitable acetalizing organic solvents are alcohols (such as methanol, ethanol, propanol, butanol or glycolether), cyclic ethers (such as tetrahydrofuran, 1,4-dioxane, 1,3-dioxolane) or dipolar aprotic solvents (such as dimethylsulfoxide, formamide,
15 N,N-dimethylformamide, hexamethyl phosphoric acid triamide or N-methylpyrrolidone).

If the acetalization is carried out in organic solvents or mixtures of organic solvents with water,
20 often the reaction product will remain in the solvent, even if the starting polyvinyl alcohol was not dissolved completely. This has the advantage that the degree of reaction can quite easily be reproduced. In order to isolate the finished product as a solid, the polymer
25 solution is introduced into a non-solvent for the polymer under stirring, filtered off and dried. As a non-solvent for the polymer e.g. acetone or methyl ethyl ketone is especially suitable.

30 Another method, which is also practicable, is to add the non-solvent for the polymer to the synthesized solution under stirring. Before the polymer is isolated as a solid, it is suitable to neutralize the catalytic acid in an appropriate step at least partially, since the
35 free base of the amino group containing polymers has the best adhesive effect in the water soluble coating. This can be carried out for instance by adding solid or dissolved organic or inorganic bases to the reaction preparation.

If the acetalization is carried out in water, for some uses, the complicated isolation by precipitation can be dispensed with and an aqueous synthesized solution can be used. Here, too, at least partial neutralization of the catalytic acid is achieved by adding solid or dissolved organic or inorganic bases to the reaction and this has a positive effect on suitable properties regarding the technical application.

10

The application of the water soluble coatings of the present invention is carried out according to processes of surface coating well-known to those of ordinary skill in the art such as doctor blade coating, roller coating, slot coating, curtain coating, injection or dipping method. Depending on the respective process employed, the basis weight per area of coating will range from 0.05 to 10 g/m².

In many cases it is suitable to apply a water soluble coating made of an aqueous solution. This has the least negative effects on the environment and on humans. For specific uses, however, it can also be suitable to use organic solvents. In some substrates the addition of from 0.5 to 60 wt.% of an organic solvent to the aqueous coating solution improves the adhesion capacity. By means of a minor solvation of the composition surface, the adhesive effect of the polymers of the coatings according to the present invention is increased further. Such additives to solvents can be, for example, alcohols or ketones.

For a proportional and quick wetting of the substrate surface, anionic, cationic or non-ionic wetting agents may be added to the coating solutions. The type and quantity are to be determined on the basis of the recommendations made by the manufacturer of such wetting agents by means of suitable tests. The quality appearance of the surface ("surface cosmetics") can

10

furthermore be influenced by adding rheological additives such as flow improvers or thickeners such as hydroxy methyl cellulose, gelatin, polyvinyl alcohol, gum arabic or polyvinyl pyrrolidone.

- 5 In order to compensate for disturbing foam formation that results from certain components of the coating solution of the invention and turbulences, as well as air in the coating process, foam separating substances such as silicone containing compounds are optionally added to the
10 coating solutions. For some uses it is also suitable to add dyes to the water soluble coating solutions for optical reasons regarding the finished product and the assessment of faults in the coating. It can also have functional reasons such as the improvement of the picture
15 quality in photostructuring processes. The dyes may be added in a dissolved or finely dispersed form.

- For specific uses the water soluble coatings can contain up to 30 wt.% of particles within the range of
20 0.05 to 50 μm , preferably 0.5 to 20 μm . This way specific optical effects such as mattness, increased mechanical strength and an improved contact with typons in vacuum printing frames when used for lithographic plates. Such particles can consist of organic substances, preferably
25 polymers, inorganic materials such as silicon dioxide, aluminium oxide etc. or inorganic substances modified organically at the surface.

- The water soluble coatings according to the
30 invention proved to be especially suitable for photosensitive layers on the basis of free radical polymerization as a result of their good adhesion and high oxygen impermeability. Preferably aqueous solutions of the water soluble coatings are applied to the
35 photosensitive layers.

The photosensitive layers consist of photo-initiators which absorb within the range of from 300 to

||

800 nm, free radical polymerizable components, as well as optional alkali soluble binders and additives.

Preferably the basic bodies and/or derivatives of
5 acetophenone, benzophenone, (trichloromethyl)-1,3,5-
triazine, benzoin, benzoin ethers, benzoin ketones,
xanthone, thioxanthone, acridine, hexarylbisimidazole or
dyes are suitable as photoinitiators for photosensitive
compositions prepared according to the invention.

10

The free radical polymerizable component of the
compound according to the invention, is an acrylic or
methacrylic acid derivative having one or more
unsaturated groups, preferably esters of the acrylic or
15 methacrylic acid in the form of monomers, oligomers or
prepolymers. It can be present as a solid or as a liquid;
solid and viscous forms are preferred. Compounds suitable
as monomers include e.g. trimethylol propane triacrylate
and methacrylate, pentaerythrit triacrylate and
20 methacrylate, dipentaerythrit monohydroxy pentaacrylate
and methacrylate, dipentaerythrite hexaacrylate and
methacrylate, pentaerythrit tetraacrylate and
methacrylate, ditrimethylol propan tetraacrylate and
methacrylate, diethylene glycol diacrylate and
25 methacrylate, triethylene glycol diacrylate and
methacrylate or tetraethylene glycol diacrylate and
methacrylate. Suitable oligomers and/or prepolymers are
urethane acrylates and methacrylates, epoxy acrylates and
methacrylates, polyester acrylates and methacrylates,
30 polyether acrylate and methacrylate or unsaturated
polyester resins.

The photoinitiators and free radical polymerizable
components may be prepared in ways known to one of
35 ordinary skill in the art. Combinations of various
photoinitiators and different free radical polymerizable
components are advantageous. The weight percentage of
the photo initiators is preferably 0.5 to 20 wt.% and
that of the free radical polymerizable components 5 to 80

17

wt.% (based on the total solid weight content of the photosensitive compositions).

Furthermore, exposure indicators e.g. belonging to the triaryl methane dyes (such as Victoria China blue BO, Victoria blue R, crystal violet) or azo dyes (such as 4-phenylazo-diphenyl-amine, azobenzene or 4-N,N-dimethyl-amino-azobenzene) can be added to the photosensitive layers. The exposure indicators are optionally present in the photosensitive mixture in an amount of from 0.02 to 10 wt.%, preferably 0.5 to 6 wt.%. Dyes for increasing the picture contrasts can be added to the photosensitive layers. Dyes which dissolve in the solvent or solvent mixture used for the coating or may be added as pigment in a dispersed form are quite suitable. The suitable contrast dyes include triphenyl methane dyes, rhodamine dyes, anthraquinone pigments and phthalocyanine dyes and/or pigments.

The photosensitive layers can furthermore optionally contain a softener. Useful softeners include dibutylphthalate, triaryl phosphate and dioctyl phthalate. Dioctyl phthalate is especially preferred. The preferred quantities of softener are 0.25 to 2 wt.%.

The water soluble coatings according to the invention are preferably suitable for producing lithographic plates. However, they may be used in recording materials for creating images on suitable carriers and receiving sheets, for creating reliefs that may serve as printing molds, screens and the like and as light hardenable varnishes for surface protection.

To produce planographic printing plates, aluminum (as the substrate) is first roughened by brushing in the dry state, brushing with abrasive suspensions or electrochemically e.g. in a hydrochloric acid electrolyte. The roughened plates, which were optionally anodically oxidized in sulfuric or phosphoric acid, are

13

then subjected to an hydrophilizing after-treatment, preferably in an aqueous solution of polyvinyl phosphoric acid, sodium silicate or phosphoric acid. The details of the above-mentioned substrate pretreatment are well-known
5 to those of ordinary skill in the art.

The dried plates are then coated with the photosensitive layers of organic solvents and/or solvent mixtures such that dry layer weight per area is
10 preferably from 0.3 to 10 g/m², more preferably 0.8 to 3 g/m². Subsequently the coating is carried out with the water soluble coating according to the invention.

The thus produced lithographic plates are exposed in
15 the common way known to the person skilled in the art. The water soluble coating can be removed separately by water and optionally mechanically by brushing prior to the development process. However, there are also uses in which the removal of the water soluble coating is
20 combined with the development step. The developed plates are usually treated with a preservative ("rubber coat"). The preservatives are aqueous solutions of hydrophilic polymers, wetting agents and other additives.

25 For specific purposes it is furthermore advantageous to increase the mechanical strength of the printing layers by means of a heat treatment or a combined use of heat and UV radiation. For this purpose, prior to this treatment the plate is first treated with a solution that
30 protects the non-image areas such that the heat treatment will cause no ink receptivity in these areas. A suitable solution is described, e.g. in U.S. Patent 4 355 096.

The following examples illustrate the specific
35 aspects of the present invention as applied to water soluble polymers used as coatings on photosensitive substrates. The examples are not intended to limit the scope thereof in any respect and should not be so construed.

14

Example 1

Preparation

5

25 g polyvinyl alcohol (Airvol 203[®], available from Airproducts, Allentown, PA; 12% residual acetal groups) are completely dissolved in 75 ml water at 60°C under stirring. After adding 6.25 g of 37% hydrochloric acid 3.42 g 2-(N-methylamino)-acetaldehyde dimethyl acetal in 25 ml water are added under stirring at 60°C within a period of 1.5 hours. These conditions are maintained for further 4 hours and subsequently a concentrated aqueous solution of 3.36 g of sodium carbonate is added drop-wise for neutralization until a pH value of 7 is obtained. The polymer is distilled off by adding acetone, filtered off and dried for 24 hours at 40°C in the circulating air dryer. By titration with 0.1 N hydrochloric acid an amino equivalent of 0.00047 mol/g is found.

Example 2

Preparation

25

25 g polyvinyl alcohol (Airvol 203[®]) are completely dissolved in 75 ml water at 60°C under stirring. After adding 4.1 g of 37% hydrochloric acid 1.15 g 4-aminobutyraldehyde dimethyl acetal in 25 ml water are added under stirring at 60°C within a period of 1.5 hours. These conditions are maintained for further 4 hours and subsequently a concentrated aqueous solution of 2.2 g of sodium carbonate is added drop-wise for neutralization until a pH value of 7 is obtained. The polymer is distilled off by adding acetone, filtered off and dried for 24 hours at 40°C in the circulating air dryer. By titration with 0.1 N hydrochloric acid an amino equivalent of 0.00026 mol/g is found.

15

Example 3

Preparation

5

25 g polyvinyl alcohol (Airvol 203® 2.6% residual acetal groups) are completely dissolved in 75 ml water at 60°C under stirring. After adding 6.25 g of 37% hydrochloric acid 3.42 g 2-(N-methylamino)-acetaldehyde dimethyl acetal in 25 ml water are added under stirring at 60°C within a period of 1.5 hours. These conditions are maintained for further 4 hours and subsequently a concentrated aqueous solution of 3.36 g of sodium carbonate is added drop-wise for neutralization until a pH value of 7 is obtained. The polymer is distilled off by adding acetone, filtered off and dried for 24 hours at 40°C in the circulating air dryer. By titration with 0.1 N hydrochloric acid an amino equivalent of 0.00026 mol/g is found.

20

Example 4

Preparation

25 g polyvinyl alcohol (Airvol 203®) are completely dissolved in 45 ml water and 45 ml n-propanol at 60°C under stirring. After adding 2.9 g of 37% hydrochloric acid 2.9 g 4-N,N-dimethylaminobenzaldehyde in 45 ml n-propanol are added under stirring at 60°C within a period of 1.5 hours. These conditions are maintained for further 4 hours and subsequently a concentrated aqueous solution of 3.36 g of sodium carbonate is added drop-wise for neutralization until a pH value of 7 is obtained. The polymer is distilled off by adding acetone, filtered off and dried for 24 hours at 40°C in the circulating air dryer. By titration with 0.1 N hydrochloric acid an amino equivalent of 0.00077 mol/g is found.

10

Example 5

A solution for a photosensitive layer is prepared
5 from the following components:

- 2.1 g terpolymer prepared by polymerization of 476
parts by weight styrene, 476 parts by weight
methyl methacrylate and 106 parts by weight
10 methacrylic acid
- 5.24 g 80% methyl ethyl ketone solution of a urethane
acrylate prepared by reacting Desmodur N100,
(available from Bayer) with hydroxy ethyl
acrylate and pentaerythritol triacrylate with
15 an amount of double bonds of 0.5 double
bonds/100g at a total reaction of isocyanate
groups
- 1.29 g dipentaerythritol pentaacrylate
- 0.6 g 2,4-trichloromethyl-6[(4-ethoxy
20 ethyleneoxy)naphtyl]1,3,5-triazine
- 0.16 g 4,4'-N,N-diethyl-amino-benzophenone
- 0.2 g benzophenone
- 0.19 g 3-mercapto-1,2,4-triazol
- 0.12 g Renol blue B2G-HW, (copper phthalocyanine
25 pigment dispersed in polyvinyl butyral
available from Hoechst)
- 0.1 g leuco Crystal Violet

These components are dissolved under stirring in 100
30 ml of a mixture comprising

35 parts by volume methyl glycol
25 parts by volume methanol
40 parts by volume methyl ethyl ketone.

35

After filtering the solution, it is applied to an
electrochemically roughened and anodized aluminum foil
that was subjected to an aftertreatment using an aqueous

17
solution of polyvinyl phosphoric acid by means of common methods and the coating is dried for 5 minutes at 90°C.

The dry weight of the printing layer amounts to approx. 2.2 g/m². Then, an oxygen-impermeable layer of 1.7 g/m² dry layer weight was applied analogously by applying a coating of an aqueous solution of the following composition:

- 10 10 g binder of preparation example 1
 150 g water

Drying also took place for 5 minutes at 95°C.

- 15 In order to assess the adherence, an adhesive tape is pressed onto the water soluble coating. When pulling off this adhesive tape, the coating is not damaged.

- 20 The printing layer is exposed under a silver film halftone step wedge having a tonal range of 0.15 to 1.95, wherein the density increments amount to 0.15, to give a negative model using a metal halogenide lamp (MH burner, available from Sack) of 10mJ/cm².

- 25 The exposed coating is treated for 30 seconds with a developer solution comprising

- 3.4 parts by weight Rewopol NLS 28,
 (available from REWO)
30 1.8 parts by weight 2-phenoxy ethanol
 1.1 parts by weight diethanol amine
 1.0 parts by weight Texapon 842,
 (available from Henkel)
 0.6 parts by weight Nekal BX Paste,
35 (available from BASF)
 0.2 parts by weight 4-toluene sulfonic acid
 91.9 parts by weight water.

16

Then the developer solution is again rubbed over the surface for another 30 seconds using a tampon and then the entire plate is rinsed with water. After this treatment the exposed portions remain on the plate. For
5 the assessment of its photosensitivity the plate is blackened in a wet state using a printing ink.

The plate's ink receptivity is good and exposed microscopic lines are very well reproduced. The gray
10 wedge is completely covered up to step 4 and partially covered up to step 7.

If between exposure and development the plates are left in the dark at room temperature for 30 minutes, the
15 same grey wedge is obtained.

For the preparation of a lithographic plate a printing layer is applied to the aluminum foil, as explained above, exposed, developed and after rinsing
20 with water the developed plate is wiped and rubbed with an aqueous solution of 0.5% phosphoric acid and 6% gum arabic. The thus prepared plate positioned in a sheet-fed offset printing machine. The ink receptivity of the plate immediately after the beginning of the printing process
25 is good. Under normal printing conditions the plate provides 200,000 copies of good quality. The plate could be used for more prints.

To simulate aging of the plates, they are stored for
30 10 days at a temperature of 40°C and 80% relative humidity. The thus treated plates are used for printing in a sheet-fed offset printing machine and exhibit no change in their printing behavior in comparison to the plates that were not artificially aged.

19

Example 6

The same photosensitive layer as in Example 5 is
5 used.

For preparing the water soluble overcoat, the
following mixture is applied:

10

10 g of the binding agent from Preparation Example 2
150 g water

Drying took place for 5 min at 95°C.

The assessment of the adhesive strength of the water
15 soluble overcoat and the exposure and development of the
printing plate is carried out as described in Example 5.

The adhesion of the overcoat is good. The ink
receptivity of the plate is good and exposed microscopic
20 lines are very well reproduced. The gray wedge is
completely covered up to step 4 and partially covered up
to step 7. If between exposure and development the plates
are left in the dark at room temperature for 30 minutes,
the same gray wedge is obtained. In a printing test,
25 200,000 copies of good quality are obtained. After this
number of copies, the printing plates were not worn and
could have been used for further printing.

30

Example 7

The same photosensitive layer as in Example 5 is
used.

35 For preparing the overcoat, the following mixture
is applied:

20

10 g of the binding agent from Preparation Example 3
150 g water

Drying took place for 5 min at 95°C.

- 5 The assessment of the adhesive strength of the water soluble overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

The adhesion of the overcoat is good. The ink
10 receptivity of the plate is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7. If between exposure and development the plates are left in the dark at room temperature for 30 minutes,
15 the same gray wedge is obtained. In a printing test, 200,000 copies of good quality are obtained. After this number of copies, the printing plates were not worn and could have been used for further printing.

20

Example 8

The same photosensitive layer as in Example 5 is used.

25

For preparing the overcoat, the following mixture is applied:

10 g of the binding agent from Preparation Example 4
150 g water

30

Drying took place for 5 min at 95°C.

- The assessment of the adhesive strength of the overcoat and the exposure and development of the printing
35 plate is carried out as described in Example 5.

21

The adhesion of the overcoat is good. The ink receptivity of the plate is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7. If between exposure and development the plates are left in the dark at room temperature for 30 minutes, the same gray wedge is obtained. In a printing test, 200,000 copies of good quality are obtained. After this number of copies, the printing plates were not worn and could have been used for further printing.

Example 9

15

The same photosensitive layer as in Example 5 is used.

For preparing the overcoat, the following mixture is applied:

20

45 g	polyvinylalcohol (Airvol 203®)
5 g	of a copolymer of 94 mol % vinyl alcohol and 5.8 mol % vinyl amine and 0.2 mol % vinylacetate with a molecular weight of 36,000
500 g	water

Drying took place for 5 min at 95°C.

The assessment of the adhesive strength of the water soluble overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

The adhesion of the overcoat is good. The ink receptivity of the plate is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7. If between exposure and development the plates are left in the dark at room temperature for 30 minutes, the same gray wedge is obtained. In a printing

12

test, 200,000 copies of good quality are obtained. After this number of copies, the printing plates were not worn and could have been used for further printing.

5

Example 10

The same photosensitive layer as in Example 5 is used.

10

For preparing the overcoat, the following mixture is applied:

42 g	polyvinylalcohol (Airvol 203®)
5 g	of a copolymer of 94 mol % vinyl alcohol and 5.8 mol % vinyl amine and 0.2 mol % vinylacetate with a molecular weight of 36,000
0.01 g	Marlophen 1028N (alkylphenolpolyethylenglycol-ether, available from Hüls)
3 g	polysilicic acid with an average particle size of 5.7 µm and a BET surface of 320 m ² /g
500 g	water

15 Drying took place for 5 min at 95°C.

The assessment of the adhesive strength of the overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

20

The adhesion of the overcoat is good. The ink receptivity of the plate is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7. If between exposure and development the plates are left in the dark at room temperature for 30 minutes, the same gray wedge is obtained. In a printing test, 200,000 copies of good quality are obtained. After this number of copies, the printing plates were not worn and could have been used for further printing.

}3

Example 11

Comparative

5

The same photosensitive layer as in Example 5 is used.

For preparing the overcoat, the following mixture
10 is applied:

50 g	polyvinylalcohol (Airvol 203®)
500 g	water

Drying took place for 5 min at 95°C.

15 The assessment of the adhesive strength of the water soluble overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

20 The adhesion of the overcoat is very poor. The adhesive tape removes almost the entire areas to which the tape adhered from the photosensitive layer. At the cutting edges the overcoat peels off.

25 The ink receptivity of the plate is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7. If between exposure and development the plates are left in the dark at room temperature for 30 minutes, the same gray wedge is
30 obtained. In a printing test, 200,000 copies of good quality are obtained. After this number of copies, the printing plates were not worn and could have been used for further printing.

35

Example 12

Comparative

34

The same photosensitive layer as in Example 1 is used.

- 5 For preparing the overcoat, the following mixture is applied:

45 g	polyvinylalcohol (Airvol 203 [®])
5 g	Polymin P (polyethylene imine, available from BASF)
500 g	water

Drying took place for 5 min at 95°C.

10

The assessment of the adhesive strength of the overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

- 15 The adhesion of the overcoat is good. The ink receptivity of the plate is good and exposed microscopic lines are very well reproduced. The plates which were subjected to simulated ageing at a temperature of 40°C and 80% relative humidity for 10 days exhibited blotchy
- 20 imperfections of the ink receptivity which did not disappear even after a larger number of copies had been printed.

Example 13

25

Comparative

The same photosensitive layer as in Example 1 is used.

- 30 For preparing the overcoat, the following mixture is applied:

50 g	polyvinyl alcohol (Airvol 203 [®])
------	--

25

450 g water
50 g ethanol

Drying takes place for 5 min at 95°C.

5 The assessment of the adhesive strength of the overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

10 The adhesion of the overcoat is poor. Large areas are removed together with the adhesive tape.

During mechanical coating by means of dipping rolls yellow components of the photosensitive layer accumulate in the dipping bath of the overcoat solution.

15 The ink receptivity of the plate is good, but exposed microscopic lines are not completely reproduced.

Example 14

20 Comparative

The same photosensitive layer as in Example 1 is used.

25 For preparing the overcoat, the following mixture is applied:

40 g polyvinyl alcohol (Airvol 203®)
30 g of a 30% dispersion of a terpolymer obtained from 66 wt.% methyl methacrylate, 29 wt.% ethyl acrylate and 5 wt.% methacrylic acid in a mixture of 90 wt.% water and 10 wt.% ethyleneglycol monomethylether
480 g water

Drying takes place for 5 min at 95°C.

)6

The assessment of the adhesive strength of the water soluble overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

5 The adhesion of the overcoat is very poor. The adhesive tape removes almost the entire areas to which the tape adhered from the photosensitive layer. At the cutting edges the overcoat peels off.

10 The ink receptivity is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 3 and partially covered up to step 6. If, however, between exposure and development the plate is left in the dark at room temperature for 30
15 minutes no image is obtained after development. This fact points to a low degree of oxygen impermeability of the overcoat. Furthermore, plates that were subjected to simulated aging at a temperature of 40°C and 80% relative humidity for 10 days showed an extension of the grey
20 wedge by 4 steps. Also in the case of the artificially aged plates, the image-free areas were not completely clean but showed a tendency towards ink receptivity.

25

Example 15

Comparative

The same photosensitive layer as in Example 5 is used.

30

For preparing the water soluble overcoat, the following mixture is applied:

48.5 g	polyvinyl alcohol (Airvol 203®)
1.5 g	glycin
500 g	water

35 Drying takes place for 5 min at 95°C.

27

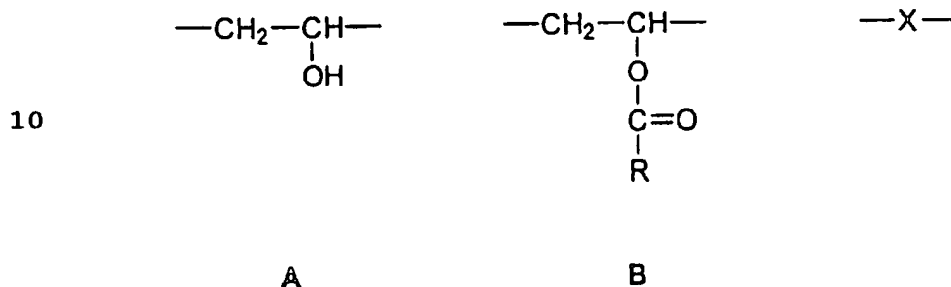
The assessment of the adhesive strength of the overcoat and the exposure and development of the printing plate is carried out as described in Example 5.

- 5 The adhesion of the overcoat is very poor. The adhesive tape removes almost the entire areas to which the tape adhered. At the cutting edges the overcoat peels off.
- 10 The ink receptivity is good and exposed microscopic lines are very well reproduced. The gray wedge is completely covered up to step 4 and partially covered up to step 7.
- 15 The present invention has been described in detail, including the preferred embodiments thereof. However, it will be appreciated that those skilled in the art, upon consideration of the present disclosure, may make modifications and/or improvements to this invention that
- 20 fall within the scope and spirit of the invention as set forth in the following claims.

28

What is claimed is:

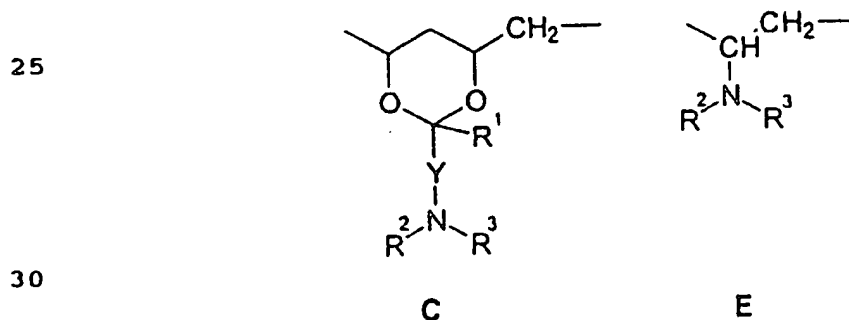
1. A coating comprising a polymer consisting of
5 the following binder units:



15

wherein R is an alkyl having 1 to 8 carbons and X comprises an amino group connected to the polymer chain either directly or via a spacer.

- 20 2. The coating according to claim 1, wherein the basic, nitrogen-containing binder unit X is at least one of structures:



35 wherein R¹, R² and R³ are independently selected from hydrogen, alkyl, aralkyl or aryl and Y is an aliphatic, aromatic or araliphatic spacer group.

3. The coating according to claim 1 wherein the polymer consists of vinyl alcohol, vinyl acetate and vinyl amine units.

40

29

4. The coating claim 2, wherein the polymer consists of vinyl alcohol and vinyl acetate units as well as unit C, wherein R^1 and R^2 are hydrogen, R^3 is a methyl and Y is a methylene bond.

5

5. The coating of claim 2 wherein the polymer consists of vinyl alcohol and vinyl acetate units as well as unit C, wherein R^1 , R^2 and R^3 are hydrogen and Y is a $-(CH_2)_4$ bond.

10

6. The coating of claim 2 wherein the polymer consists of vinyl alcohol and vinyl acetate units as well as unit D, wherein R^1 is hydrogen, R^2 and R^3 are a methyl and Y is a 1,4-phenylene bond.

15

7. The coating of claims 2 wherein the polymer consists of 10 to 98 wt.% unit A, 0.1 to 30 wt.% unit B and 0.1 to 60 wt.% unit C.

20

8. The coating of claim 1 additionally comprising at least one other polymer consisting of vinyl alcohol and vinyl acetate groups and/or at least one common additive.

25

9. The coating of claim 8 wherein the additive is selected from a wetting agent, a solid having particle sizes of between 0.05 and 25 μm , rheological additives, foam separators, dyeing agents, stabilizers and/or preservatives.

30

10. The use of the polymer in claim 1 as a binder.

11. The use of the polymer in claim 1 for producing a coating for light-sensitive systems.

35

12. The use according to claim 11 wherein the light-sensitive system comprises at least one free radical-forming photoinitiator or mixtures of photo initiators and coinitiators that sensitize the mixture

30

for the wave lengths of from 300 to 800 nm as light-sensitive component, at least one alkali-soluble, carboxyl group-containing binder, free radically polymerizable components having unsaturated groups as
5 well as further additives.

13. The use of the polymer of claim 1 for producing a lithographic printing plate coating.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 97/17761

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08F8/12 C09D129/04 C09D131/02 G03F7/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08F C09D G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	PATENT ABSTRACTS OF JAPAN vol. 004, no. 038 (C-004), 27 March 1980 & JP 55 012171 A (SEKISUI CHEM CO LTD), 28 January 1980, see abstract ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 004, no. 050 (C-007), 16 April 1980 & JP 55 023163 A (AGENCY OF IND SCIENCE & TECHNOL), 19 February 1980, see abstract ---	1
X	PATENT ABSTRACTS OF JAPAN vol. 011, no. 048 (M-561), 13 February 1987 & JP 61 211081 A (KURARAY CO LTD), 19 September 1986, see abstract ---	1
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex

Special categories of cited documents

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

3 February 1998

Date of mailing of the international search report

13/02/1998

Name and mailing address of the ISA

European Patent Office, P. B. 5816 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040. Tx 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Schueler, D

INTERNATIONAL SEARCH REPORT

Int. l. Application No

PCT/US 97/17761

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	PATENT ABSTRACTS OF JAPAN vol. 097, no. 003, 31 March 1997 & JP 08 310123 A (FUJI PHOTO FILM CO LTD), 26 November 1996, see abstract ---	1
X	US 2 748 103 A (PRIEST) 10 June 1952 see column 1, line 47 - line 51 ---	1
X	EP 0 339 371 A (AIR PROD & CHEM) 2 November 1989 see page 3: figure 1 ---	1
X	EP 0 627 656 A (AGFA GEVAERT AG) 7 December 1994 see examples P1,P3,P8 ---	1
X	EP 0 632 096 A (WACKER CHEMIE GMBH) 4 January 1995 see examples N-PVA11,-2,-3 ---	1
P,X	EP 0 752 430 A (SUN CHEMICAL CORP) 8 January 1997 see claims 1-4 ---	1,10,11
P,X	EP 0 752 622 A (MINNESOTA MINING & MFG) 8 January 1997 see claims 1,7 ---	1
P,X	EP 0 757 061 A (SUN CHEMICAL CORP) 5 February 1997 see claims 1-4,9,10 ---	1,10,11
X	DE 40 34 543 A (AIR PROD & CHEM) 2 May 1991 see claim 11 ---	1
X	DE 43 25 015 A (AGFA GEVAERT AG) 2 February 1995 see examples P15,P17,P22 ---	1
X	DE 195 16 435 A (AIR PROD & CHEM) 16 November 1995 see tables -----	1,10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/17761

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2748103 A	29-05-56	NONE	
EP 0339371 A	02-11-89	CA 1330684 A DE 68912388 D DE 68912388 T JP 1923541 C JP 2011609 A JP 6051741 B US 5155167 A	12-07-94 03-03-94 11-05-94 25-04-95 16-01-90 06-07-94 13-10-92
EP 0627656 A	07-12-94	DE 4318438 A JP 7013282 A US 5455154 A	08-12-94 17-01-95 03-10-95
EP 0632096 A	04-01-95	DE 4321070 A AT 131849 T CA 2126586 A CN 1103876 A DE 59400066 D ES 2081723 T FI 942979 A JP 7041632 A US 5567750 A	05-01-95 15-01-96 25-12-94 21-06-95 01-02-96 01-03-96 25-12-94 10-02-95 22-10-96
EP 0752430 A	08-01-97	DE 19524851 A CA 2180581 A US 5700619 A	09-01-97 08-01-97 23-12-97
EP 0752622 A	08-01-97	US 5534381 A JP 9118718 A	09-07-96 06-05-97
EP 0757061 A	05-02-97	DE 19525050 A CA 2180580 A US 5698360 A	30-01-97 11-01-97 16-12-97
DE 4034543 A	02-05-91	US 5155167 A CA 2028365 A GB 2237572 A,B JP 3160004 A	13-10-92 01-05-91 08-05-91 10-07-91

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 97/17761

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 4325015 A	02-02-95	NONE	
DE 19516435 A	16-11-95	US 5519093 A	21-05-96
		CA 2148660 A	12-11-95
		GB 2289280 A	15-11-95
		JP 7304833 A	21-11-95